Phase Equilibria in Fe-Cu-X (X: Co, Cr, Si, V) Ternary Systems

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Phase equilibria on the Fe-Cu side in the Fe-Cu-X (X: Co, Cr, Si, V) system were experimentally determined over the temperature range of 1073-1273 K. Based on the present results and previous works, the thermodynamic assessments of the phase equilibria in the Fe-Cu-X system were evaluated using the Calculation of Phase Diagram (CALPHAD) method. The Gibbs energies (*G*) of the bcc, fcc, and liquid phases are described by the subregular solution model, and a set of thermodynamic parameters enable us to calculate various isothermal and vertical sections and the miscibility gaps of the solid and liquid phases.

1. Introduction

Copper has been used widely as an alloying element in the steel industry to improve strength by aging and to improve corrosion resistance. Recently, it has been reported that a new Fe-Cu-based alloy containing Al has been developed as a glass die material [1995Tan]. Despite many advantages resulting from the presence of Cu in ferrous alloys, Cu has a negative aspect, that is, it induces hot shortness (cracking) during rolling. In addition, from an environmental point of view, Cu pickup from steel scrap is a problem for the recycling process because it is difficult to remove Cu in the steel-melting process.

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Table 1 Equilibrium Composition of the Fe-Cu-Co System

Temperature, K	Equilibria Phase 1/Phase 2	Composition, wt.% Phase 1 Cu	Phase 1 Co	Phase 2 Cu	Phase 2 Co
1073	(Cu)/α-Fe	95.27	0.11	3.10	1.81
		96.44	0.22	2.39	4.20
		95.12	0.44	3.21	6.61
		94.71	0.68	3.14	9.97
1173	(Cu)/γ-Fe	97.09	0.13	6.00	1.81
		96.62	0.30	6.62	3.98
		95.74	0.52	7.46	6.20
		94.98	0.87	8.01	9.32
1273	(Cu)/γ-Fe	94.43	0.13	8.69	1.54
		94.71	0.26	9.08	3.72
		93.35	0.84	9.42	6.13
		93.36	0.84	9.17	9.26

Phase equilibria in the Fe-Cu-based alloys are of importance for the development of Fe-Cu-based alloys and for their possible use in the recycling process. The Fe-Cu binary phase diagram reviewed by Okamoto [1993Oka] is shown in Fig. 1, where the calculated metastable miscibility gap of the liquid phase is included [1995Che]. Several studies on the metastable miscibility gap of the liquid phase in the Fe-Cu binary system have been performed [1958Nak, 1997Wil, 1999Ama].

An investigation of the solid/liquid equilibria in Fe-Cu-based ternary systems has been carried out by this group previously [1997Oht, 2000Wan]. As a continuation, the purpose of the present work is to investigate experimentally the effect of alloying elements on the solid/solid phase equilibria in the Fe-Cu-based alloys and to conduct thermodynamic assessments on the basis of the experimental data to construct a thermodynamic database of phase equilibria for Fe-Cu-based alloys using the CALPHAD method.

Table 2 Equilibrium Composition of the Fe-Cu-Cr System

Temperature, K	Equilibria Phase 1/Phase 2	Composition, wt.% Phase 1 Cu	Phase 1 Cr	Phase 2 Cu	Phase 2 Cr
1073	(Cu)/α-Fe	95.16	0.08	2.95	1.66
		96.12	0.11	3.54	3.22
		95.88	0.22	2.92	6.41
		97.96	0.22	3.23	10.10
1173	(Cu)/γ-Fe	94.83	0.12	5.30	1.68
		96.06	0.17	5.13	3.24
		96.32	0.19	4.48	6.58
		97.10	0.21	4.19	10.79
1273	(Cu)/γ-Fe	95.29	0.05	6.53	1.68
		94.83	0.13	6.51	3.13
		95.02	0.27	5.26	6.65
		94.84	0.49	4.34	10.85
1473	Liquid/γ-Fe	96.77	0.12	3.38	9.20

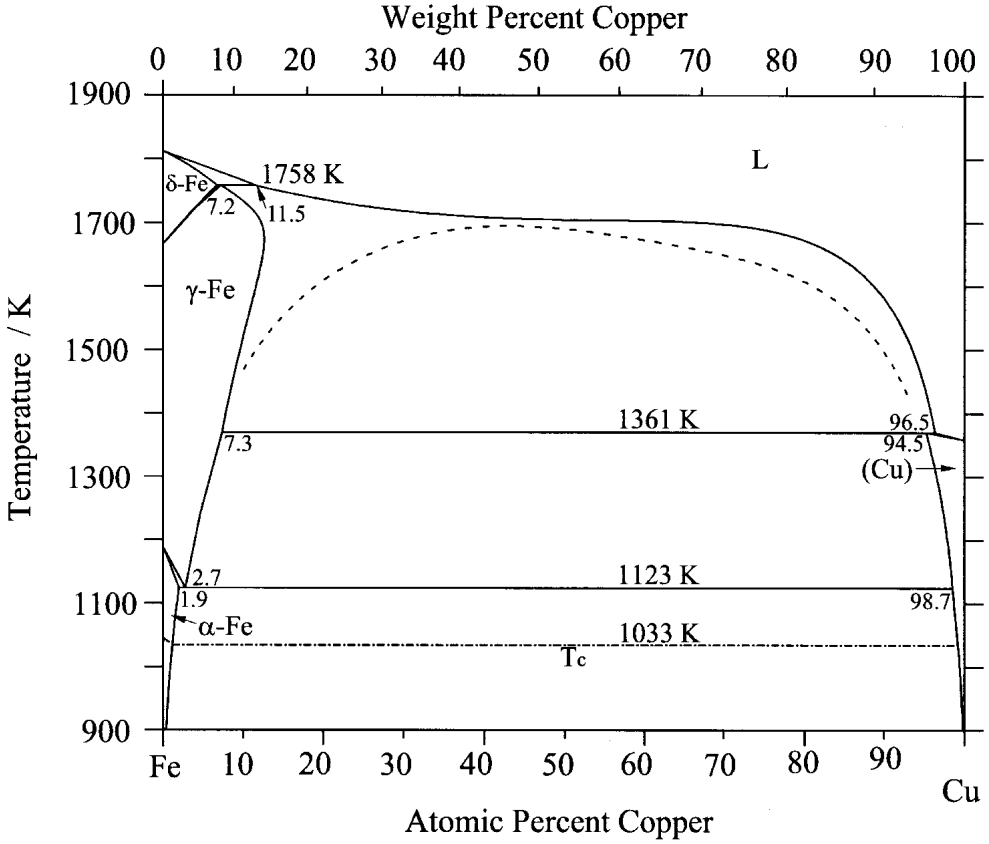

Fig. 1 Fe-Cu phase diagram compiled by Okamoto [1993Oka]

Table 3 Equilibrium Composition of the Fe-Cu-Si System

Temperature, K	Equilibria Phase 1/Phase 2	Composition, wt.% Phase 1 Cu	Phase 1 Si	Phase 2 Cu	Phase 2 Si
1073	(Cu)/α-Fe	94.16	0.25	3.22	1.77
		94.03	0.28	3.38	3.51
		96.79	0.33	2.26	6.98
		97.03	0.61	1.33	11.33
		96.13	2.04	1.41	14.18
		95.23	3.27	1.99	15.06
		92.23	3.70	1.98	15.91
1173	(Cu)/α-Fe	92.25	0.13	3.99	1.67
		94.65	0.28	4.13	3.43
		96.16	0.51	2.91	6.89
		96.50	0.75	2.40	10.49
		96.18	2.17	2.86	14.05
		94.72	3.81	3.87	15.29
		94.16	3.96	3.52	15.64
1273	Cu/γ-Fe	93.51	0.22	7.77	1.71
	(Cu)/α-Fe	94.19	0.38	5.35	3.70
		95.09	0.61	4.42	6.40
		96.74	1.05	3.24	10.06
		95.92	2.16	3.16	13.74

Table 4 Equilibrium Composition of the Fe-Cu-V System

Temperature, K	Equilibria Phase 1/Phase 2	Composition, wt.% Phase 1 Cu	Phase 1 V	Phase 2 Cu	Phase 2 V
1073	(Cu)/α-Fe	95.04	0.07	3.00	1.73
		95.89	0.08	3.31	3.33
		96.83	0.10	1.86	7.12
		96.89	0.22	1.80	11.46
1173	(Cu)/α-Fe	94.26	0.04	4.92	1.66
		95.38	0.07	3.37	3.30
		96.90	0.08	2.57	7.48
		97.70	0.09	2.43	11.42
1273	(Cu)/α-Fe	93.97	0.04	6.44	1.68
		94.56	0.10	4.71	3.39
		95.89	0.12	3.95	7.10
		95.12	0.30	3.28	10.94

2. Determination of Phase Equilibria

2.1 Experimental Procedure

Fe-Cu-(1-12 wt.%) X (X: Co, Cr, Si, V) (Fe:Cu = 1:1 wt.%) alloys were prepared in alumina crucibles by melting electrolytic copper (99.99 wt.%), iron (99.95 wt.%), and alloying elements (X) with a purity of 99.9% or more in a

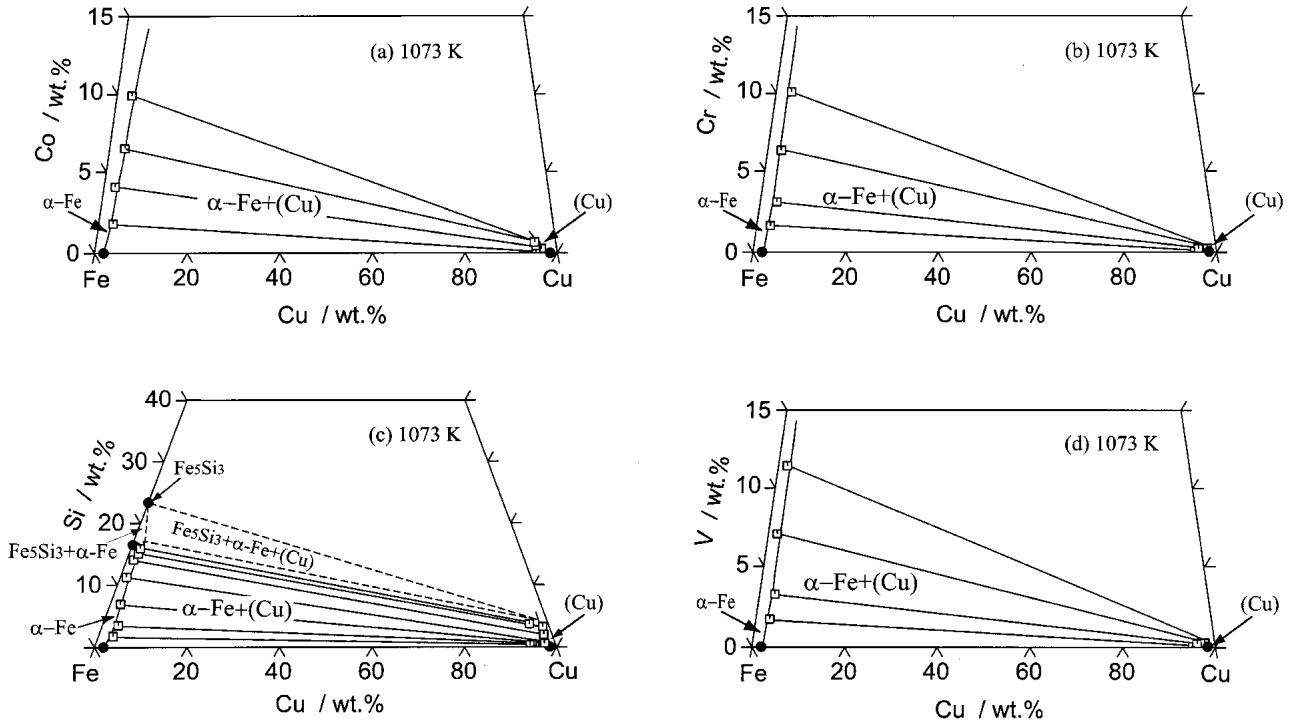

Fig. 2 Isothermal section diagrams of the Fe-Cu portion at 1073 K in the **(a)** Fe-Cu-Co, **(b)** Fe-Cu-Cr, **(c)** Fe-Cu-Si, and **(d)** Fe-Cu-V systems. ⊡, Present work; ●, Data of binary system

Table 5 Assessed Fe-X and Cu-X Binary Systems Used in the Present Calculation

Fe-X	Reference	Cu-X	Reference
Fe-Cu	[1995Che]	Cu-Co	[2000Kub]
Fe-Co	[1988Gui]	Cu-Cr	[1990Ham]
Fe-Cr	[1987And]	Cu-V	[1990Ham]
Fe-V	[1991Hua]	Cu-Si	[1998Buh]
Fe-Si	[1991Lac]		

high-frequency induction furnace under an argon atmosphere. The alloy ingots were hot-rolled at approximately 1173 K down to sheets of about 2.5 mm thickness and then solution-treated at 1173 K for 24 h. The specimens were sealed in transparent quartz capsules and heat-treated at 1073-1273 K for 336-1680 h and then quenched in iced water. Equilibrium compositions of each phase were determined by SEM-Electron Dispersive X-Ray (EDX) analysis using a standard calibration method. It was confirmed that the specimens are shown to reach the equilibrium state because the compositions of each phase in alloys are almost same.

2.2 Experimental Results

The phase equilibria in the Fe-Cu side in the Fe-Cu-X (X: Co, Cr, Si, V) system at 1073, 1173, and 1273 K were determined, and the equilibrium compositions were listed in Tables 1-4. As an example, the phase equilibria in the Fe-Cu side of the Fe-Cu-X system at 1073 K are shown in Fig. 2 (a-d). Figure 3 classifies the types of phase equilibria on the Fe-Cu side of the Fe-Cu-X system by summarizing the present and previous works [1995Vil1,2, 1998Wan, 2000Wan]. Mn, Ni, and Al have almost the same distribution behavior ($K_x = W_x^{\alpha-Fe \text{ or } \gamma-Fe}/W_x^{(Cu) \text{ or } L} \approx 1$) between the α-Fe or γ-Fe and (Cu) or L phases, and a wide range of solid solution is formed when these elements are added to a certain amount as shown in Fig. 3(a). From Fig. 3(b) and (c), it is seen that, although $K_x > 1$ for the addition of Co, Cr, Si, V, these elements have little solubility in the Cu-rich phase, but have a certain solubility in the Fe-rich phase. Figure 3(d) shows that Mo and Nb have very little solubility in both the Cu-rich and Fe-rich phases. When small amounts of Mo and Nb are added to the Fe-Cu system, the λ (Fe_2Mo) and ϵ (Fe_2Nb) intermetallic phases appear [2000Wan].

3. Thermodynamic Calculation

3.1 Thermodynamic Model

The thermodynamic model for calculating the phase equilibria in this work is based on the subregular solution model with the Redlich-Kister formula [1948Red]. The G of the liquid, bcc, and fcc phases in ternary Fe-Cu-X system are described as follows:

$$G_m^{\phi} = {}^0G_{Cu}^{\phi}x_{Cu} + {}^0G_{Fe}^{\phi}x_{Fe} + {}^0G_x^{\phi}x_x + RT(x_{Cu}\ln x_{Cu} + x_{Fe}\ln x_{Fe} + x_x \ln x_x) + L_{CuFe}^{\phi}x_{Cu}x_{Fe} + L_{CuX}^{\phi}x_{Cu}x_x + L_{FeX}^{\phi}x_{Fe}x_x + L_{CuFeX}^{\phi}x_{Cu}x_{Fe}x_x + G^{mag} \quad \text{(Eq 1)}$$

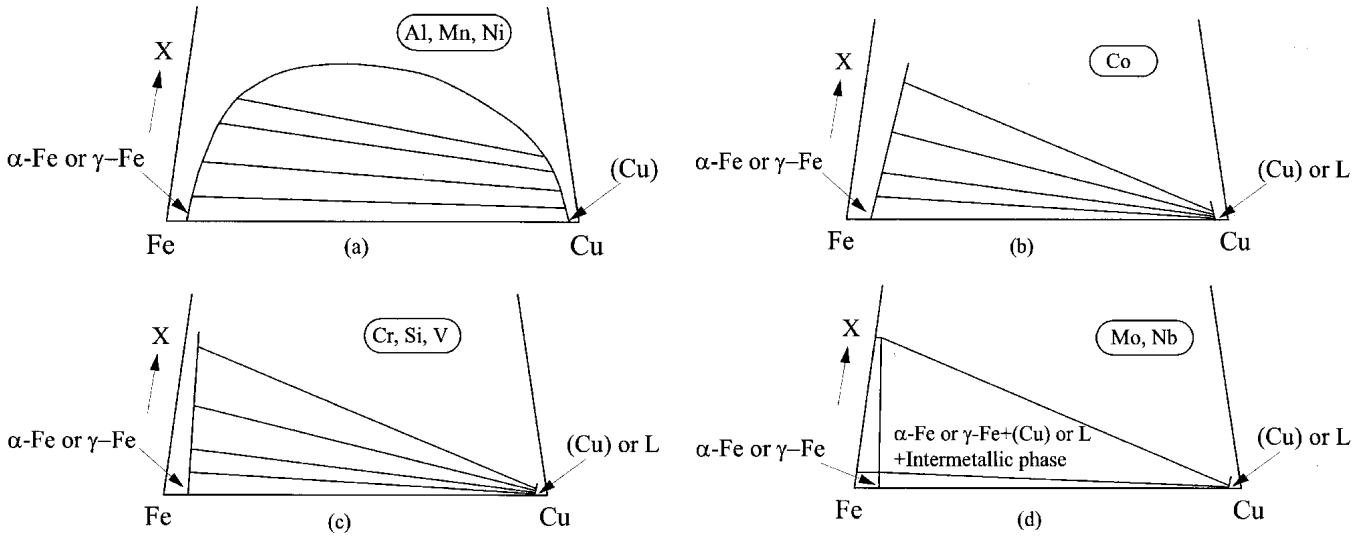

Fig. 3 Classification of phase equilibria of the Fe-Cu portion in the Fe-Cu-X system

Table 6 Evaluated Thermodynamic Parameters in the Fe-Cu-X Ternary Systems

System	Phase	Thermodynamic Parameters, J/mol	Reference
Fe-Cu-Co	Liquid	${}^{0}L^{L}_{CuFeCo} = 22000$	This work
		${}^{1}L^{L}_{CuFeCo} = -32000$	
		${}^{2}L^{L}_{CuFeCo} = -1500$	
	fcc	${}^{0}L^{fcc}_{CuFeCo} = -35327.7 + 8 \cdot T$	This work
		${}^{1}L^{fcc}_{CuFeCo} = -87000 + 58 \cdot T$	
		${}^{2}L^{fcc}_{CuFeCo} = -93000 + 50 \cdot T$	
	bcc	${}^{0}L^{bcc}_{CuFeCo} = {}^{1}L^{bcc}_{CuFeCo} = {}^{2}L^{bcc}_{CuFeCo} = -155000 + 75 \cdot T$	This work
Fe-Cu-Cr	Liquid	${}^{0}L^{L}_{CuFeCr} = {}^{1}L^{L}_{CuFeCr} = {}^{2}L^{L}_{CuFeCr} = 0$	[1997Oht]
	fcc	${}^{0}L^{fcc}_{CuFeCr} = {}^{1}L^{fcc}_{CuFeCr} = {}^{2}L^{fcc}_{CuFeCr} = 35007.5 - 27.5 \cdot T$	This work
	bcc	${}^{0}L^{bcc}_{CuFeCr} = {}^{1}L^{bcc}_{CuFeCr} = {}^{2}L^{bcc}_{CuFeCr} = 38650 - 50 \cdot T$	[1997Oht]
Fe-Cu-Si	Liquid	${}^{0}L^{L}_{CuFeSi} = {}^{2}L^{L}_{CuFeSi} = 23000 - 19.5 \cdot T$	This work
		${}^{1}L^{L}_{CuFeSi} = 50000 - 19.5 \cdot T$	
	fcc	${}^{0}L^{fcc}_{CuFeSi} = {}^{1}L^{fcc}_{CuFeSi} = {}^{2}L^{fcc}_{CuFeSi} = -231494.5 + 130 \cdot T$	This work
	bcc	${}^{0}L^{bcc}_{CuFeSi} = {}^{2}L^{bcc}_{CuFeSi} = -158642.5 + 50 \cdot T$	This work
		${}^{1}L^{bcc}_{CuFeSi} = -182105.5 + 70 \cdot T$	
Fe-Cu-V	Liquid	${}^{0}L^{L}_{CuFeV} = -85000$	This work
		${}^{1}L^{L}_{CuFeV} = 5000$	
		${}^{2}L^{L}_{CuFeV} = -80000$	
	fcc	${}^{0}L^{fcc}_{CuFeV} = {}^{1}L^{fcc}_{CuFeV} = {}^{2}L^{fcc}_{CuFeV} = -30000$	[1997Oht]
	bcc	${}^{0}L^{bcc}_{CuFeV} = {}^{1}L^{bcc}_{CuFeV} = {}^{2}L^{bcc}_{CuFeV} = 30000 - 25 \cdot T$	This work

where ${}^{0}G_{i}^{\Phi}$ is the molar G of the pure component i with the ϕ phase, which is taken from the lattice stability value for the pure element compiled by [1991Din], and x_i is the mole fraction of component i. L_{ij}^{Φ} is the interaction parameter between i and j atoms, and L_{CuFeX}^{Φ} is the ternary interaction parameter. The temperature and composition dependence of the parameters L_{ij}^{Φ} and L_{CuFeX}^{Φ} are expressed in the following forms:

$$L_{ij}^{\phi} = {}^{0}L_{ij}^{\phi} + {}^{1}L_{ij}^{\phi}(x_i - x_j) + {}^{2}L_{ij}^{\phi}(x_i - x_j)^2 + {}^{3}L_{ij}^{\phi}(x_i - x_j)^3 + \ldots = \sum_{m=0}^{n} {}^{m}L_{ij}^{\phi}(x_i - x_j)^m \quad \text{(Eq 2)}$$

$$ {}^{m}L_{ij}^{\phi} = {}^{m}A + {}^{m}BT + {}^{m}CT\ln T \quad \text{(Eq 3)}$$

$$L_{CuFeX}^{\phi} = A' + B'T \quad \text{(Eq 4)}$$

G^{mag} is the magnetic contribution of the G, which is described by Eq 5 [1978Hil]:

$$G^{mag} = RT\ln(\beta + 1) f(\tau) \quad \text{(Eq 5)}$$

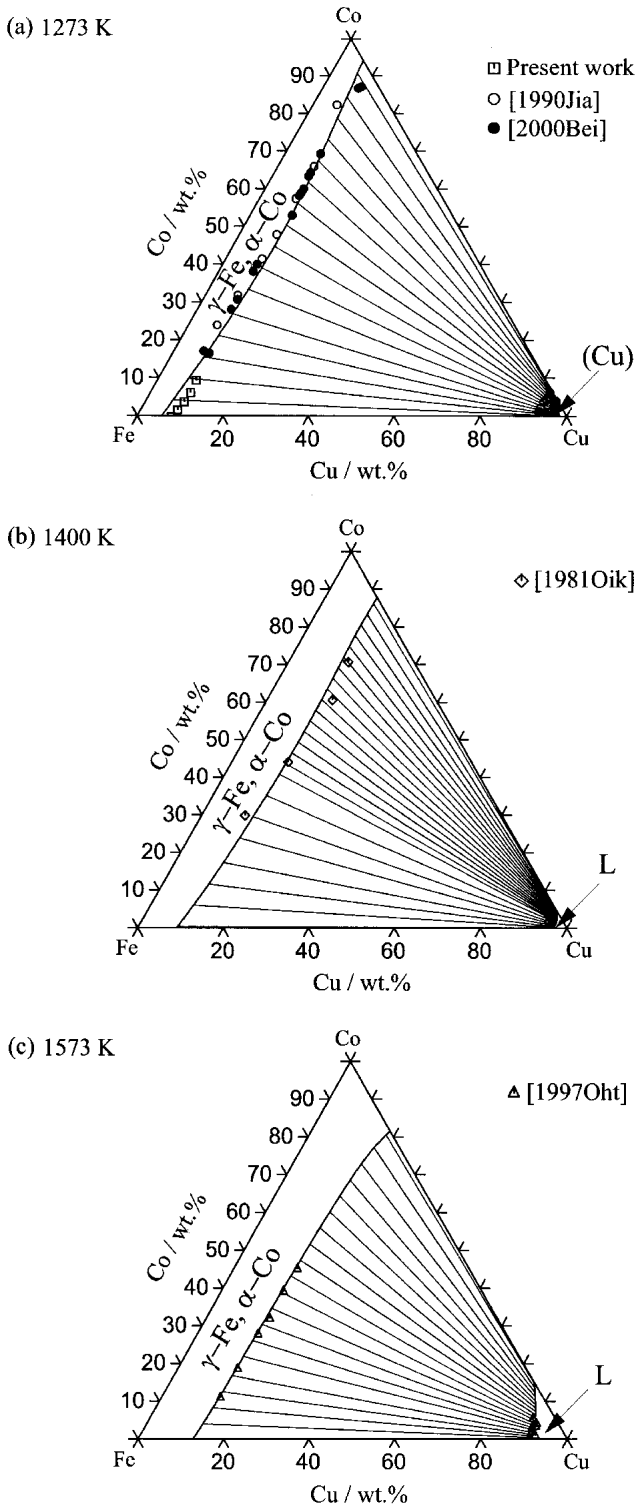

Fig. 4 Calculated isothermal section diagrams of the Fe-Cu-Co system at **(a)** 1273 K, **(b)** 1400 K, and **(c)** 1573 K

The function $f(\tau)$ is formulated by the polynomial of the normalized temperature, τ, where τ is defined as T/T_c^{Φ}. T_c^{ϕ} is the Curie temperature of solution for ferromagnetic ordering and β is the Bohr magnetron number.

Due to a lack of experimental information on the intermetallic phases in the Fe-Cu-X ternary system, solubilities of the intermetallic phases in ternary systems are not considered in the present assessment.

3.2 Calculation of Phase Diagram

The thermodynamic assessments of each binary system reported in previous works are used in the present work and are listed in Table 5. On the basis of the present and previous data [1997Oht], the ternary thermodynamic parameters of the Fe-Cu-X system were optimized as summarized in Table 6. Details of the assessment for each ternary system are shown as follows:

Fe-Cu-Co System. Some vertical section diagrams using thermal analysis and metallography have been reported [1936Jel, 1936Mad]. Based on these results, Raghavan [1992Rag1] reviewed the phase equilibria of this system and constructed the isothermal sections at 1073, 1173, and 1273 K. Some isothermal section diagrams have been reported at 1273 K [1990Jia], 1150 K, 1200 K, 1300 K, 1400 K, 1450 K, 1550 K [1981Oik], and at 1373 K, 1473 K, and 1573 K [1997Oht]. Most recently, the metastable liquid miscibility gap in the Fe-Cu-Co alloys has been investigated by Kim [2000Kim], where the critical temperatures of the metastable liquid miscibility gap within the error range of ±10 K were determined at various concentrations, and Bein et al. [2000Bei] calculated the phase diagrams at 1073-1273 K using the Cluster Variation Method.

The present thermodynamic assessment was made on the basis of these experimental data. The calculated isothermal section diagrams at 1273 K, 1400 K, and 1573 K are shown in Fig. 4(a-c). The vertical sections at Fe:Co = 1:1 wt.%, 10, 20, 30 wt.% Co, and 10, 20 wt.% Fe, including the metastable miscibility gap of the liquid phase, are shown in Fig. 5(a-f). The calculated metastable miscibility gaps of the liquid phase are shown in Fig. 6 at different temperatures. It is seen from Fig. 5 and 6 that the calculated results of the metastable miscibility gap of the liquid phase are in good agreement with the experimental data [2000Kim].

Fe-Cu-Cr System. The isothermal section diagrams at 1373 K, 1523 K [1967Sal], 1273 K [1993Hao], and 1373 K, 1473 K, and 1573 K [1997Oht] in this system were determined, whereas some vertical section diagrams also were reported [1939Mor, 1970Ahm].

The present thermodynamic assessment was carried out above 1073 K on the basis of the present and previous works. The calculated isothermal sections at 1273 K, 1373 K, and 1573 K are shown in Fig. 7 in comparison with the experimental data.

Fe-Cu-Si System. Vogel and Horstmann [1953Vog] studied phase equilibria in the ternary Fe-Cu-Si system and determined the quasi-binary section of FeSi-Cu_3Si using thermal analysis and microstructure observation. According to their experimental results, Chang et al. [1979Cha] and Raghavan [1992Rag2] reviewed the phase equilibria in the Fe-Cu-Si ternary system. Very recently, new experimental investigations of the liquid/solid- and liquid/liquid-phase equilibria have been undertaken on the ba-

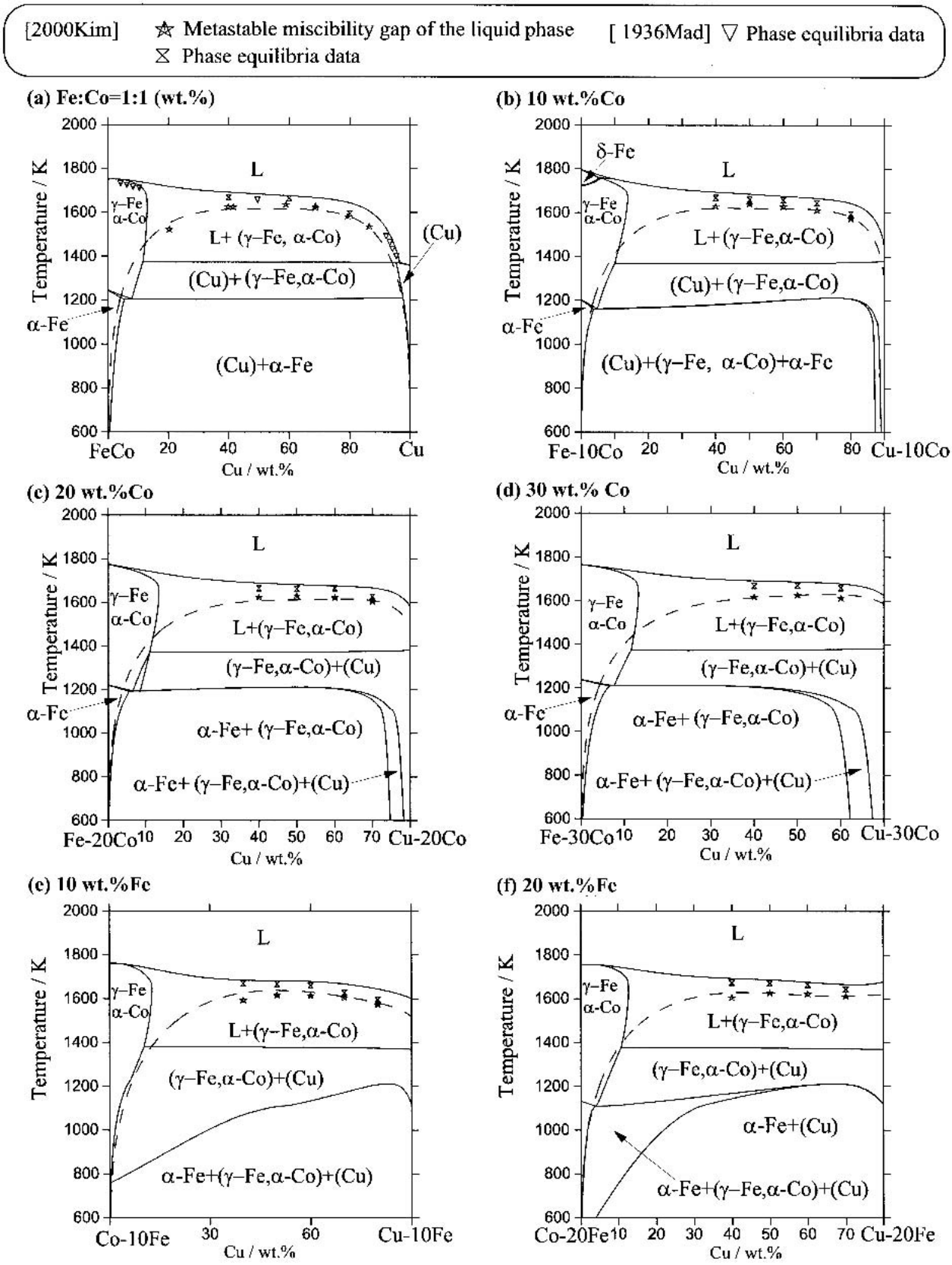

Fig. 5 Calculated **(a)** Fe/Co = 1:1 (wt.%); **(b)** 10 wt.% Co; **(c)** 20 wt.% Co; **(d)** 30 wt.% Co; **(e)** 10 wt.% Fe; and **(f)** 20 wt.% Fe vertical section diagrams, including the metastable miscibility gap of the liquid in the Fe-Cu-Co system. ——, Phase boundary; – – –, Metastable miscibility gap of the liquid

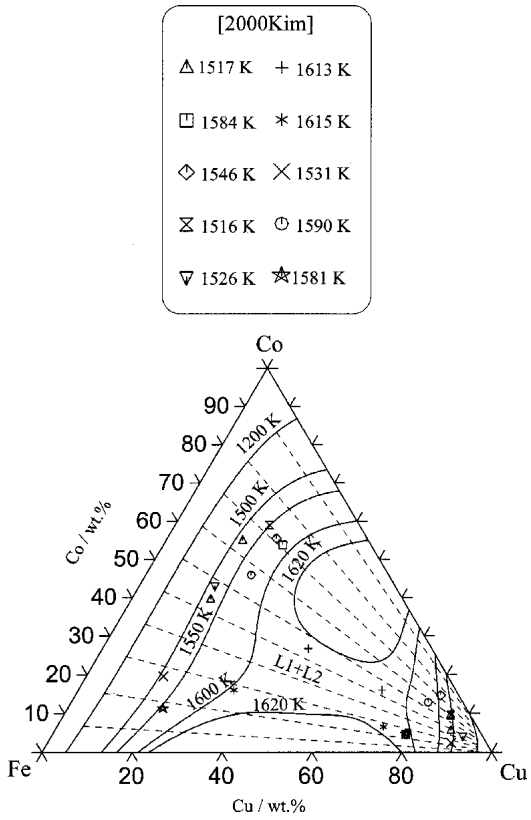

Fig. 6 Calculated metastable miscibility gap of the liquid phase in the Fe-Cu-Co system

sis of the diffusion couple method [1997Oht] and EPMA analysis [1999Hin], respectively. Hino et al [1999Hin] determined the phase boundary of the miscibility gap of the liquid phase, which is larger than that reported elsewhere [1979Cha, 1992Rag2].

A thermodynamic assessment above 1373 K was made by [1997Oht, 1999Hin], respectively, in which the thermodynamic assessment of the Cu-Si binary system reported by Lüdecke [1987Lud] was used. However, the lattice stabilities of pure elements used in the Cu-Si binary system [1987Lud] were not consistent with those of the Scientific Group Thermodata Europe [1991Din]. Recently, a reassessment of the binary Cu-Si system was made by Bühler et al. [1998Buh] with the CALPHAD method that was used in the present thermodynamic assessment. As an example, the calculated isothermal section diagrams of the Fe-Cu-Si ternary system at 1173 K, 1573 K, and 1723 K are shown in Fig. 8, where the experimental data are included for comparison.

Fe-Cu-V System. Because previous thermodynamic data on the Fe-Cu-V system are not available, the present assessment was made based on the investigation of the liquid/solid-phase equilibria reported by Ohtani et al. [1997Oht] and the present results. The calculated isothermal sections at 1173 K, 1373 K, and 1573 K are shown in Fig. 9 in comparison with the experimental data.

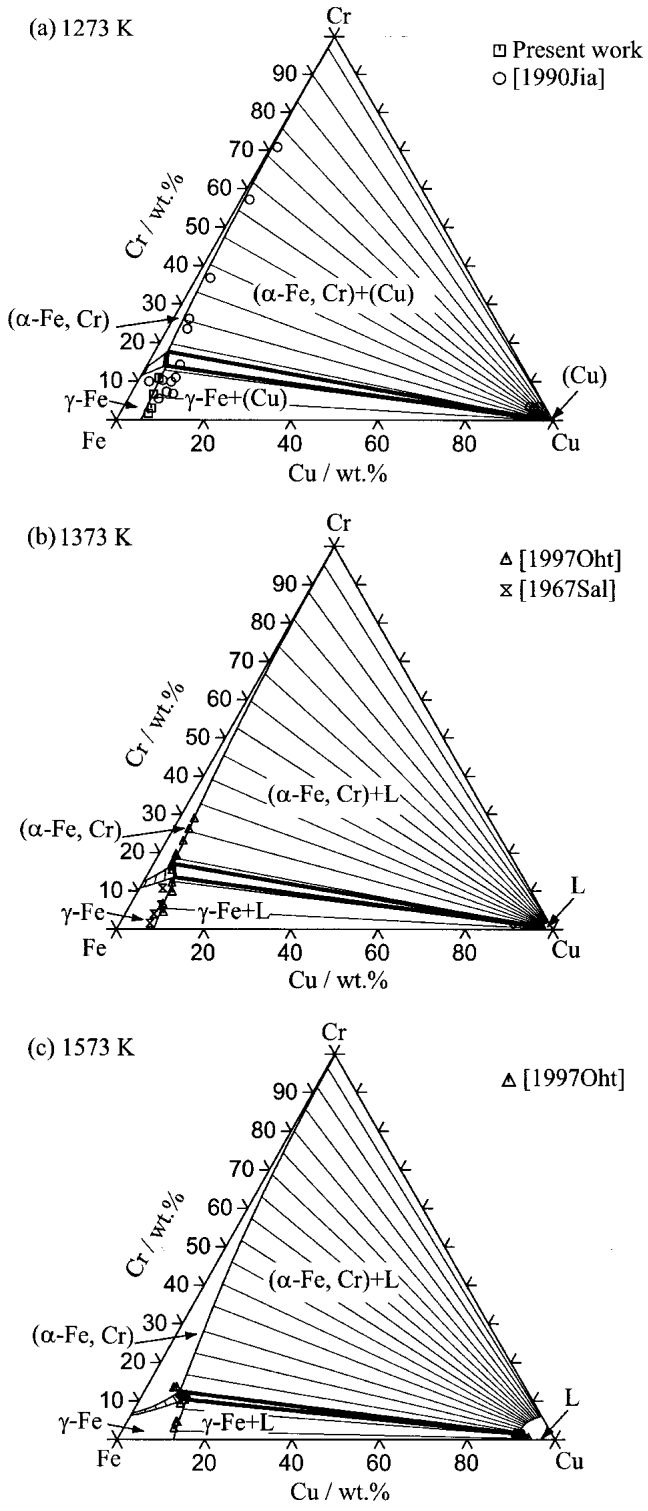

Fig. 7 Calculated isothermal section diagrams of the Fe-Cu-Cr system at **(a)** 1273 K, **(b)** 1373 K, and **(c)** 1573 K

3.3 Miscibility Gap of the Liquid Phase

As mentioned above, the metastable miscibility gap of the liquid phase exists in the Fe-Cu binary system. The effect of alloying elements on the miscibility gap of

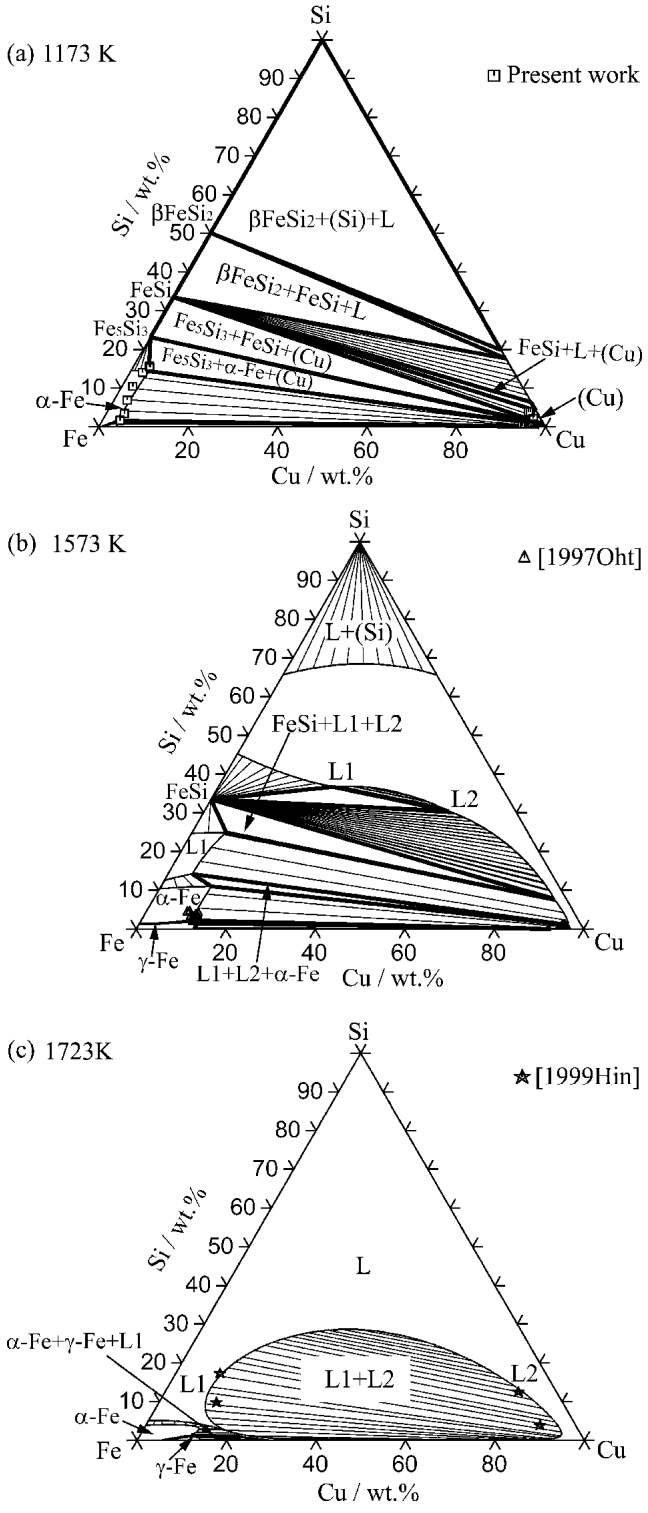

Fig. 8 Calculated isothermal section diagrams of the Fe-Cu-Si system at **(a)** 1173 K, **(b)** 1573 K, and **(c)** 1723 K

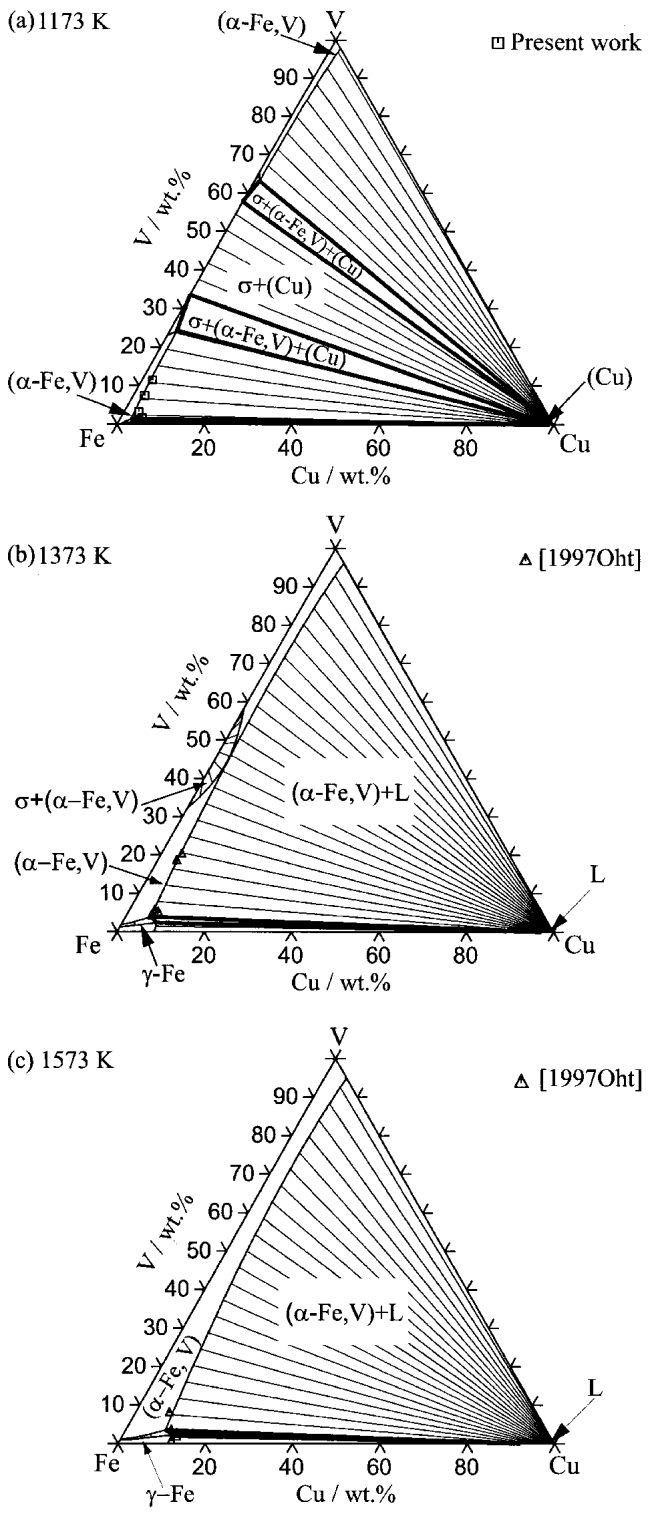

Fig. 9 Calculated isothermal section diagrams of the Fe-Cu-V system at **(a)** 1173 K, **(b)** 1373 K, and **(c)** 1573 K

the liquid phase in the Fe-Cu system can be evaluated. Figure 10 shows the stable and metastable miscibility gaps of the liquid phase in the Fe-Cu-X system, where different types of miscibility gaps of liquid phase appear in the Fe-Cu-X system. It can be seen from Fig. 6 and Fig. 10(a) and (b) that the tie-lines in the Fe-Cu-Co, Fe-Cu-Cr, and Fe-Cu-V systems lie along the Cu-FeCo, Cu-FeCr, and Cu-FeV directions. This can be qualitatively explained as

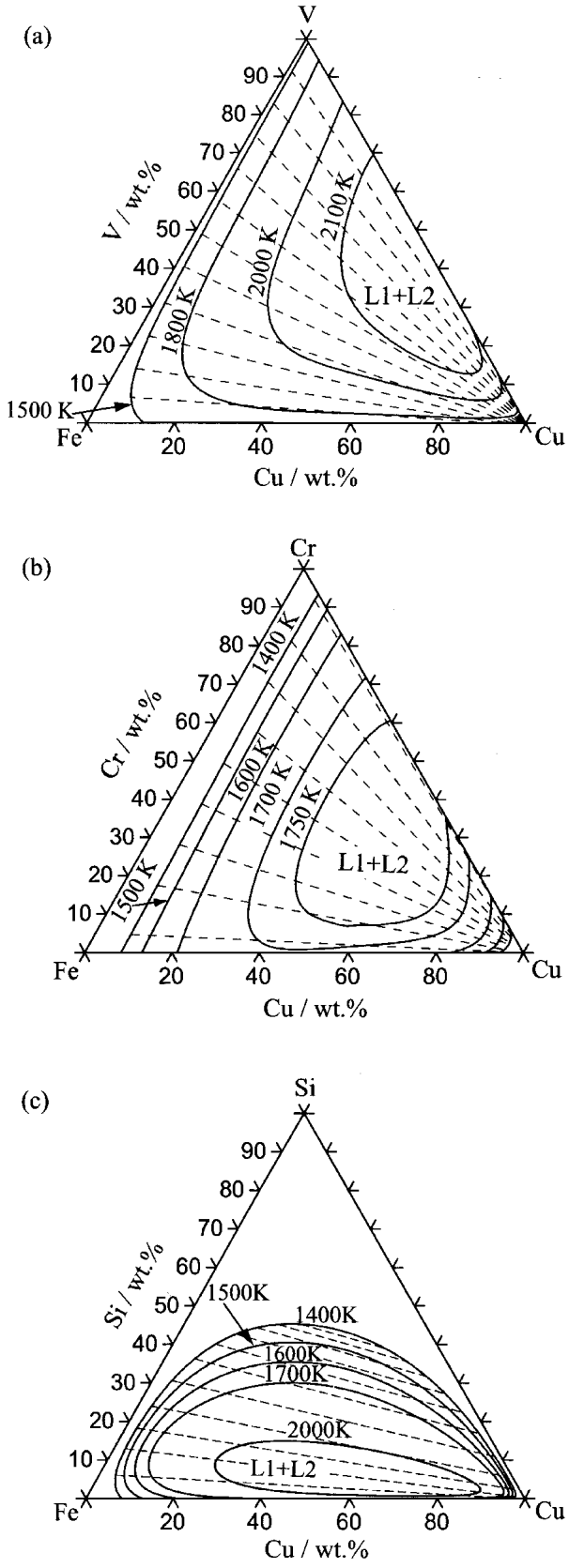

Fig. 10 Calculated miscibility gap of the liquid phase in the **(a)** Fe-Cu-V system, **(b)** Fe-Cu-Cr system, and **(c)** Fe-Cu-Si system

being due to the enthalpy of mixing in the binary systems. According to the semi-empirical values of mixing enthalpies of the liquid [1983Nie], the following relations are obtained:

$$\Delta H_{CuFe}(+53) > \Delta H_{CuCr}(+51) > \Delta H_{FeCr}(-6)\ (kJ/mol)$$

$$\Delta H_{CuFe}(+53) > \Delta H_{CuV}(+21) > \Delta H_{FeV}(-29)\ (kJ/mol)$$

$$\Delta H_{CuFe}(+53) > \Delta H_{CuCo}(+26) > \Delta H_{FeCo}(-2)\ (kJ/mol)$$

Because repulsion forces exist between Cu and Fe, Cr, and Co or V and attractive forces exist between Fe and Cr, and Co or V, the tie-lines radiate from the Cu corner to the Fe-Cr, Fe-Co or Fe-V sides. On the other hand, the tie-lines in the Fe-Cu-Si system lie along the CuSi-FeSi direction, as shown in Fig. 10(c). In this case, the mixing enthalpies of the liquid are as follows:

$$\Delta H_{CuFe}(+53) >> \Delta H_{CuSi}(-40) > \Delta H_{FeSi}(-75)\ (kJ/mol)$$

Because repulsion forces exist between Cu and Fe and the attractive forces between Fe or Cu and Si, the tie-lines radiate from the Cu-Si side to the Fe-Si side in the Fe-Cu-Si system.

4. Conclusions

In conclusion, the phase equilibria in the Fe-Cu side were determined in the Fe-Cu-X (X: Co, Cr, Si, V) system in the temperature range from 1073-1273 K. Thermodynamic assessments of phase diagrams in Fe-Cu-X ternary system were performed above 1073 K, and good agreement was obtained between the calculated and experimental data including the miscibility gap of the liquid phase.

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